6

POLARISED ELECTRONIC SPECTRA OF SINGLE CRYSTALS OF PARA DICHLOROBENZENE

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Plate I

ABSTRACT. The polarisation of the ultraviolet absorption spectra of very thin single crystals of *p*-dichlorobenzene has been studied by photographing simultaneously the two components with the light vector respectively parallel to the *b*-axis and the *c*-axis. It is observed that although the bands due to $0 \rightarrow v$ transitions are equally sharp in the vertical and horizontal components the 0, 0 band is sharp only in the vertical component, but it has a triplet structure in the horizontal component. Analysis of the bands in the horizontal component shows that an intermolecular vibration of frequency about 53 cm^{-1} is coupled with the 0, 0 transition only in this component and also two other new $0 \rightarrow v$ transitions not observed in the vertical component take place in this component. It is pointed out that these vibrational transitions occur when the light vector is along the short axis of the molecule and they always appear in the vapour.

The identical positions of some of the bands due to $0 \rightarrow v$ transitions in both the components indicate that there is no Davydov splitting in this case. The expected Davydov splitting due to interaction of nearest neighbours has been calculated and found to be 22 cm^{-1}. Such a splitting could be easily detected. The absence of this splitting is explained on the assumption that the usual expression for the mean square transition moment cannot be used in this case, because only a few nearest neighbouring molecules are effective in producing the splitting, and the oscillator strength being very low, the mean moment is derived from the absorption by a large number of molecules.

INTRODUCTION

It was observed by Craig and Hobbins (1955) that in the two components of the ultraviolet absorption band system of single crystal of anthracene with the light vectors respectively parallel and perpendicular to the *b*-axis the component with light vector parallel to the *b*-axis consists of two bands at 2680Å and 2595Å respectively, but in the other component the bands shift to 2300Å. They calculated the shift expected on the theory put forward by Davydov (1948) and found that the calculated values were in agreement with the experimental results.

The crystal of *p*-dichlorobenzene has a structure similar to that of anthracene with two molecules in the unit cell and the orientations of these molecules in the lattice have been found out accurately by Croatto *et al.* (1952). It would,

therefore, be quite easy to extend the calculations on Davydov's theory to this particular crystal. It was formerly observed by Swamy (1953) that the near ultraviolet absorption band system of polycrystalline mass of *p*-dichlorobenzene at −180°C consists of sharp bands and there is no indication of presence of a second system slightly displaced from the first system in this spectrum, as would be expected if the two components were slightly displaced from each other On the other hand, in the case of *o*-dichlorobenzene at −180°C the band system indicated a splitting of each band into three components widely separated from each other, and later, Roy and Sirkar (1957) observed that when the molecules of *o*-dichlorobenzene are dispersed in frozen alcohol at −180°C no such splitting occurs. These results indicate that the splitting is produced by the interaction of the permanent dipoles in the crystal on the transition moments

In the case of *p*-dichlorobenzene crystals it was difficult to come to a definite conclusion regarding the absence of the splitting, because if one of the two components were very much weaker than the other it would be difficult to separate the two components from each other in the spectrum due to the polycrystalline mass. So, it was thought worthwhile to study the polarisation of the ultraviolet band system of *p*-dichlorobenzene to find out the structure and relative positions of the two systems. It was also intended to calculate the splitting expected on Davydov's theory in this case.

EXPERIMENTAL

Very thin single crystals of *p*-dichlorobenzene were prepared from saturated solutions in alcohol at room temperature The crystal elongated along *c*-axis was mounted with its *c*-axis vertical between two fused silica discs in a brass frame, the lower portion of which was immersed in liquid oxygen contained in a Dewar vessel of fused silica. The crystal was held with its *bc*-face normal to the incident rays from a hydrogen discharge tube and the light transmitted by the crystal was focussed on the slit of a Hilger large quartz spectrograph with a fused silica lens. A double-image prism of quartz was used to separate the components having light vectors vertical and horizontal respectively.

Microphotometric records of the spectra were taken with a Kipp and Zonen type self-recording microphotometer and before taking the records of the two components, a linear mark parallel to a prominent iron line in the iron arc comparison spectrum was made by cutting across both the components of the spectrum with a sharp razor blade. The mark produced a very narrow peak in the microphotometric record and distances of the sharp bands in the records of the two components of the spectrum from this mark could be measured very accurately. The dispersion in the record was about 2Å or 24 cm^{-1} per mm in the region of 2800Å. A shift of the sharp bands larger than 6 cm^{-1} could be easily measured by this method.

RESULTS AND DISCUSSION

(a) *Assignment of the bands*

The vertical and horizontal components of the polarised electronic absorption spectrum are reproduced in figure 1 and the microphotometric records of the bands are shown in figure 2 in Plate I. The frequencies of the bands in the vertical and horizontal components are given in Table I. Care was taken to measure the distance of the bands from the mark *F* mentioned earlier. The frequencies of the bands due to the vapour reported by earlier workers are also included in the table.

It can be seen from figure 2 that although the bands on the shorter wavelength side of the 0,0 band are equally sharp in both the vertical and horizontal components, the 0, 0 band in the horizontal component is much broader than that in the vertical component. Table 1 shows that the bands at 36051 cm^{-1} and 36247 cm^{-1}

TABLE 1

Polarised absorption bands of *p*-dichlorobenzene

Vapour (Sponer, 1942) for comparison		Light vector parallel to *c*-axis		Light vector parallel to *b*-axis	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
35783 vs	0, 0(ν_0)	35672 s	0 0(ν_0)	35629 s	ν_0--53
				35672 s	0,0(ν_0)
36070 m	ν_0+357	36051 vw	ν_0+379	35725 s	ν_0+53
				36051 w	ν_0+379
36274 ms	ν_0+431	36247 m	ν_0+575	36111 m	ν_0+439
				36247 m	ν_0+575
36438 m	ν_0+695	36419 m	ν_0+747	36366 m	ν_0+694
36471 s	ν_0+728	36539 w	ν_0+867		
36544 w	ν_0+801	36736 s	ν_0+1064		
36808 vs	ν_0+1065	36930 w	ν_0+1258		
36998 m	ν_0+1255	37172 m	ν_0+2×750		
37069 w	ν_0+801+531	37308 m	ν_0+1064+572		
37136 w	ν_0+1065+327	37489 m	ν_0+1064+753		
37205 vw	ν_0+2×731	37601 w	ν_0+1064+865		
37340 vw	ν_0+1065+531	37804 s	ν_0+2×1066		
37546 m	ν_0+1065+728	37994 m	ν_0+1064+1258		
37856 vs	ν_0+2×1065	38229 m	ν_0+1064+2×747		
38040 w	ν_0+1065+695 +531	38547 m	ν_0+2×1067+747		
38195 w	ν_0+2×1065+327	38853 s	ν_0+3×1060		
38274 ms	ν_0+1065+2×728				
38602 w	ν_0+2×1065+728				
38937 s	ν_0+3×1065				

are present in both the components exactly at same positions. So there is no shift of these bands in the horizontal component from the positions of the corresponding bands in the vertical component by more than 6 cm^{-1}, which is the maximum probable error in the measurement. The bands at 36111 cm^{-1} and 36366 cm^{-1} in the horizontal component are quite strong, but they are absent in the vertical component. Careful examination of the 0, 0 band in the horizontal component shows that it consists of two adjacent peaks separated by about 80 cm^{-1}, one of the bands being twice as broad as the other. If it is assumed that this structure is produced by splitting of the energy level into two components, the other bands due to $0 \rightarrow v$ transitions cannot be assigned properly. On the other hand, if it is assumed that the 0, 0 band in this case is at the same position as in the vertical component some of the excited state frequencies given by the bands at 36051 cm^{-1} and 36247 cm^{-1} are found to be exactly the same as those given by the corresponding bands in the vertical component as shown in Table I. The remaining bands in the horizontal component are found to be missing in the vertical component and these bands give some new excited state frequencies 439 cm^{-1} and 694 cm^{-1} as shown in Table I.

The structure of the 0, 0 band in the horizontal component can be explained on the assumption that when the light vector is parallel to the *b*-axis some intermolecular vibration of frequency 53 cm^{-1} is coupled to the electronic transition, but when the vector is along the *c*-axis no such coupling takes place. Actually both $v \rightarrow 0$ and $0 \rightarrow v$ transitions produce strong bands on the two sides of the 0,0 band. Further, the appearance of the new bands in the horizontal component can also be explained by assuming that in this case some new modes of vibration are excited, but they are not excited when the light vector is along the *c*-axis and makes a large angle with the short axis of the molecule.

It can be seen from Table I that the excited state vibrational frequencies deduced from the bands in the horizontal component all agree with those observed in the case of the vapour, but some of these bands are absent in the vertical component. It appears, therefore, that the vibrations of excited state frequencies 439 cm^{-1} and 694 cm^{-1} are excited only when the lightvector is almost parallel to the short axis of the molecule. In the vapour the molecules have random orientation and therefore, all the modes of vibration are excited. This information given by the polarised spectra may be helpful in assigning the vibration frequencies of the molecule unequivocally.

(b) *Search for the Davydov splitting*

The splitting of the 0,0 band expected from Davydov's theory has been calculated in this case for the molecules in the *bc*-plane taking into account only the interaction of nearest neighbours.

If A be the value of interaction integral for interaction between translationally equivalent molecules along *a*-axis, B that between similar molecules along

Fig 1. Polarised electronic spectrum of single crystals of *p*–dichlorobenzene at –180°C, with light vector (a) parallel to *c*–axis, (b) parallel to *b*–axis.

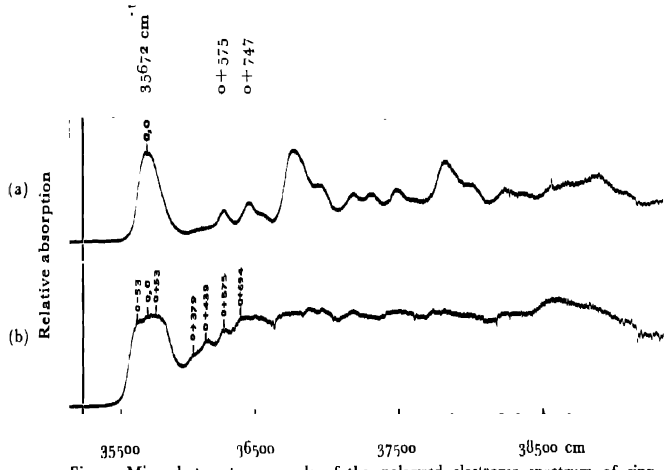

Fig 2. Microphotometric records of the polarised electronic spectrum of sing crystals of *p*–dichlorobenzene at –180°C, with light vector (a) parallel to *c*–axis, (b) parallel to *b*–axis.

b-axis and C that for interaction between the two molecules in the unit cell, the splitting between the two components is given by $8C$. Actually it has been shown by Davydov (1948) that if only dipole-dipole interaction is taken into account, the interaction integral I_{lk} is given by

$$I_{lk} = -\left(\frac{e^2}{r_{lk}^3}\right) |M|^2 \{2\cos\theta_{l1}\cos\theta_{k1} - \cos\theta_{l2}\cos\theta_{k2} - \cos\theta_{l3}\cos\theta_{k3}\} \quad \ldots \quad (1)$$

where θ_{l1}, θ_{l2} and θ_{l3} are angles made by the transition moment of the l-th molecule with the three rectangular axes, M is the molecular transition moment and r_{lk} the distance between the centres of the two molecules. The values of A, B and C calculated from eqn.(1) are given in Table II for the p-dichlorobenzene crystal. The unit is cm^{-1} and that for $|M|$ is Å.

TABLE II

	Long axis-transition	Short axis-transition
$A/\|M\|^2$	−48	25
$B/\|M\|^2$	613	−1771
$C/\|M\|^2$	−407	−170

As the component parallel to b-axis is more strongly absorbed than the other component, and the molecule is inclined at 62°C to the b-axis the transition in this particular case is a short-axis one. Hence the splitting expected is $1360\,|M|^2$. The value of $|M|^2$ can be found out from that of f, the oscillator strength from the relation

$$|M|^2 = \frac{3hf}{8\pi^2 mc\nu} \quad \ldots \quad (2)$$

where c is the velocity of light, h the Planck's constant, m, the electronic mass and ν the frequency of the band in cm^{-1}. The value of f can be obtained from the relation

$$f = 2.3 \times \frac{nc^2 m}{N\pi e^2} \; 10^3 \int \epsilon d\nu \quad \ldots \quad (3)$$

where n is the refractive index, N the Avogadro number and ϵ is given by the relation

$$\epsilon = \left(\frac{1}{\mathbf{c}d}\right) \log_{10} (I_0/I)$$

$\mathbf{c}$ being the concentration in moles per litre.

The values of $\int \epsilon d\nu$ for solutions of p-dichlorobenzene and benzene were reported by Conrad-Billroth (1932) and subtracting the value of $\int \epsilon d\nu$ for benzene

from that for *p*-dichlorobenzene we get the oscillation strength for the migration in the ring in the *p*-dichlorobenzene molecule. The value of f is found to be 6.4×10^{-3}, and this leads to a value 16.3×10^{-3} Å^2 for $|M|^2$. Hence, the splitting expected in the case of *p*-dichlorobenzene is about 22 cm^{-1}. The bands in the horizontal component should shift towards red relative to those in the vertical component by about 22 cm^{-1}. As mentioned earlier, such a splitting is not actually observed in figures 1 and 2.

The discrepancy mentioned above may be due to two alternative causes. *First, the value of oscillator strength calculated from the extinction coefficients reported by Conrad-Billroth (1932) may be a little too high. But if it is assumed* that the value of f is not far from the true value, the alternative cause of the discrepancy may be the non-applicability of the expression for the transition moment in this particular case. It can be seen that in Davydov's theory it is assumed that all the neighbouring molecules have the transition moment produced simultaneously, the magnitude of this moment being determined by the probability of excitation and is taken as the mean transition moment. Such an assumption will lead to a correct value to extinction coefficient, because a large number of molecules is contained in a small volume. In calculating the influence of the neighbouring dipoles on the transition moment, however, we are concerned only with the molecules in a few unit cells and a correct value of the mean square transition moment in this case cannot be given by the theory. It may so happen that when a molecule is excited none of its nearest neighbours is excited simultaneously and when the oscillator strength is very low there is high probability of occurrence of such an event. This may produce a horizontal component undisplaced from its original position. When the oscillator strength is high there is high probability of simultaneous excitation of the neighbouring molecules in a few unit cells, and therefore, the theoretical values of the splitting may agree with the observed values as in the case of anthracene (Craig and Hobbins, 1955).

It is quite clear, however, that when the transition takes place in the field of permanent dipoles a large splitting occurs, as in the case of *o*-dichlorobenzene. As the crystal structure of *o*-dichlorobenzene has not been determined yet with sufficient accuracy it is not possible to calculate the splitting on Davydov's theory